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Covering the period May 1, 1976 to October 31, 1976

NOVEL DUPLEX VAPOR-ELECTROCHEMICAL METHOD FOR SILICON SOLAR CELLS

By: Vijay K. Kapur and L. Nanis

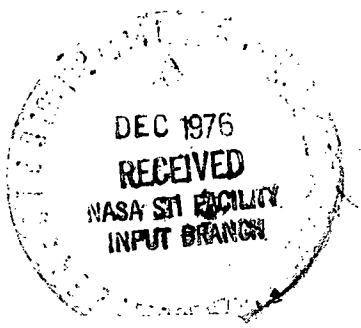
Prepared for:

JET PROPULSION LABORATORY
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91103

Attn: Dr. Ralph Lutwack
Spacecraft Power Station

Contract No. 954471 under NAS 7-100
SRI Project PYU 4980

STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.



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Approved:

P. J. Jorgensen, Acting Director
Materials Research Center

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SUMMARY

- Silicon can be produced by the reduction of SiF_4 gas with sodium in a reaction that initiates at temperatures lower than 175°C.
- The kinetics of the reaction can be affected by varying the partial pressure of SiF_4 gas.
- Emission spectrographic analysis of product silicon shows the major impurity to be sodium; but the metallic impurities that are known to degrade solar cell efficiency, such as Ti, V, Zr, Cr, were not detected and must be less than 10 ppm.

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INTRODUCTION

This second quarterly report of contract 954471 describes the progress made on the project during the period May 1, 1976 to October 31, 1976.

In this project, we are trying to develop a two-step process for the production of low-cost solar grade silicon. The steps are:

(1) Reduce silicon tetrafluoride gas (SiF_4) with an alkali metal such as sodium to produce high-purity silicon.

(2) Further purify the silicon obtained in Step 1 by the formation and subsequent disproportionation of SiF_2.

The two-step process can be described chemically as:

Step 1: $$SiF_{4(g)} + 4\ Na \rightarrow Si + 4NaF \qquad (1)$$

Step 2: $$Si + SiF_{4(g)} \underset{500\text{-}750^{\circ}C}{\overset{1100^{\circ}C}{\rightleftharpoons}} 2SiF_{2(g)} \qquad (2)$$

Currently we are working on Step 1 of this process to establish optimum conditions for the reaction between SiF_4 and Na to give high-purity silicon.

As reported in our first quarterly report,* the results of our preliminary experiments show that silicon is produced as a brown powder-like substance when the reaction between SiF_4 gas and sodium metal is initiated at 325°C. Na_2SiF_6 is also formed as a reaction product, according to the reaction

$$2NaF + SiF_{4(g)} \rightarrow Na_2SiF_6 \qquad (3)$$

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* First Quarterly report of this project, August 1976

It was also reported that silicon could be separated from the reaction products by leaching the sodium fluorides with hot water.

In order to perform the reaction in Eq. (1) under controlled conditions, apparatus was designed and constructed to permit SiF_4 purification and transfer into a reactor, as described in this report.

EXPERIMENTAL

Because both SiF_4 and Na are air sensitive, the reaction between them can be carried out only in an inert atmosphere. A glass vacuum line suitable for the multiple operations required for Step 1 was set up as shown in Fig. 1. The vacuum line has a modular construction and can be quickly assembled and disassembled for cleaning or modification.

The main parts of the vacuum line are identified in Fig. 1 as:

(A) SiF_4 purification unit

(B) SiF_4 storage bulbs

(C) Detachable reaction kettle assembly.

Some other notable features of this vacuum line are that the entire system is constructed with greaseless stopcocks and greaseless joints, and that no mercury manometers are used. The vacuum measurements are made with thermocouple gauges (F in Fig. 1), and the pressure measurements are made with a precision solid-state pressure transducer.

SiF_4 Purification

The most commonly found impurities in SiF_4 gas are air and SO_2.* These are removed by passing SiF_4 gas over heated iron (800°C) in a quartz tube. SiF_4 is further purified by fractional distillation on the vacuum line (A in Fig. 1) by condensing the gas in a series of cold traps at selected temperatures.

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* P. L. Timms, R. A. Kent, T. C. Ehlert & J. L. Margrave, J. Am. Chem. Soc. 87, 2824 (1965).

Figure 1

MODULAR CONSTRUCTION VACUUM LINE

(A) SiF_4 Purification Unit

(B) SiF_4 Storage Bulbs

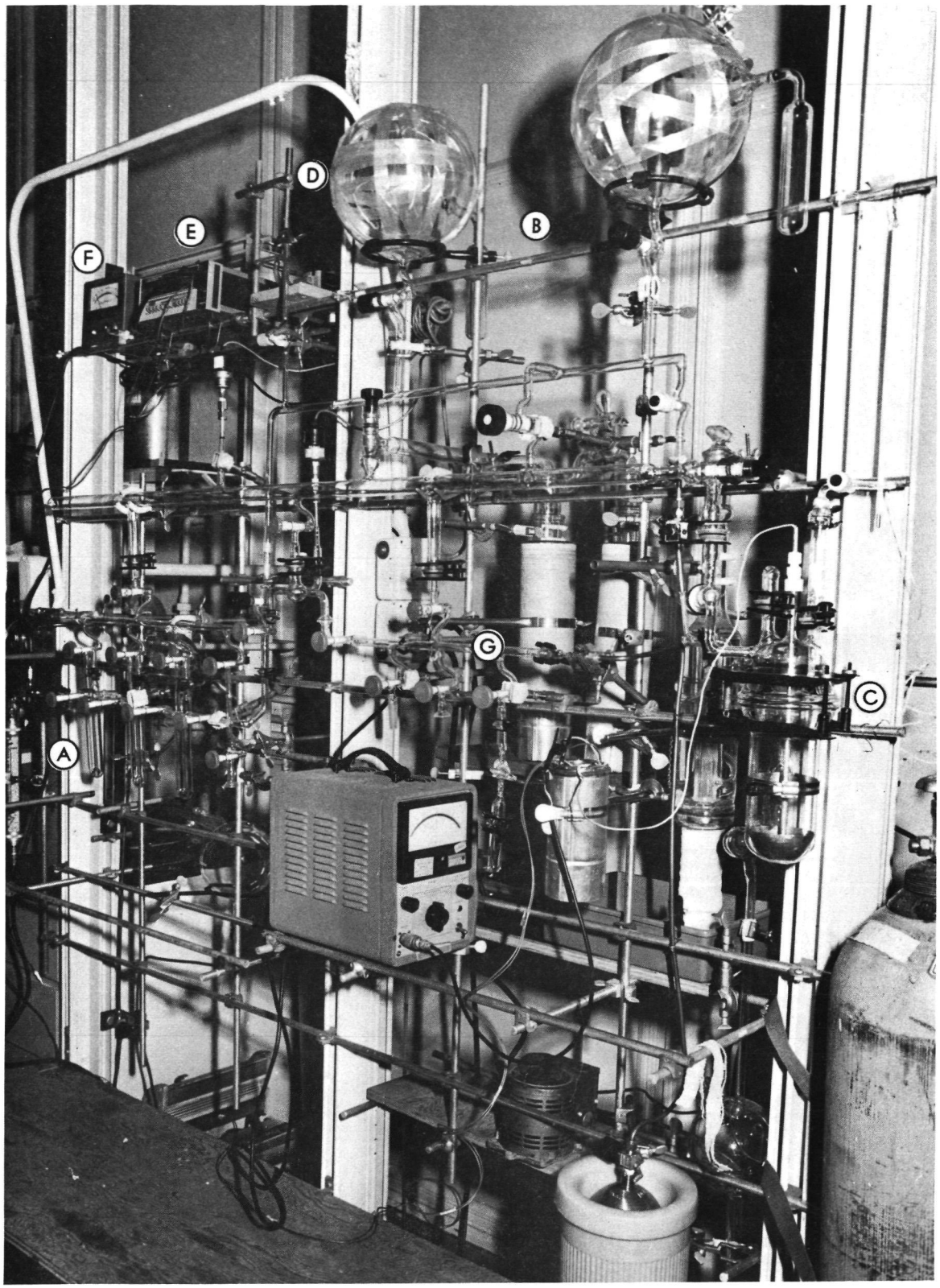
(C) Detachable Reaction Assembly

(D) Solid State Pressure Transducer

(E) Digital Multimeter

(F) Thermocouple Gauge

(G) Multipurpose Vacuum Connections



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SiF_4 Storage

Purified SiF_4 is stored in two glass bulbs, each with a nominal capacity of 5.8 liters (B in Fig. 1). These storage bulbs are connected to a pressure transducer (Unimeasure-80, D in Fig. 1). This device conveniently measures pressure in the range 0 to 1.4 atm. The only part of this device that contacts SiF_4 gas is a precision diaphragm made of NiSpan-C alloy, through stainless steel tubing, 1/16 in. diameter. A change of gas pressure in the system causes displacement in the transducer, allowing the pressure change to be read as a change in resistance (digital multimeter, E in Fig. 1).

The pressure transducer was calibrated in a range of 0 to 1.3 atm, giving a linear relation between pressure and resistance. From the slope of this linear relation, a scale factor of $\frac{\Delta\Omega \text{ (ohm)}}{\Delta P \text{ (mmHg)}} = 2.84$ was obtained. The resistance change is read on a digital multimeter with 4-1/2 digits so that a change of 0.1Ω can be accurately resolved. In other words, a pressure change in the system by 0.284 mmHg can be accurately sensed by the transducer.

To measure the moles of SiF_4 removed from the storage bulbs (Δn), the gas law $\frac{V\Delta P}{RT} = \Delta n$ is used. For this calculation, an accurate measure of the volume of the bulbs is necessary. The volume was calibrated by filling the evacuated bulbs with ultrapure CO_2 and noting the pressure and temperature. CO_2 was then removed from the bulbs into an evacuated, preweighed container and solidified by cooling with liquid nitrogen. The weight of CO_2 removed from the bulbs was determined as the difference in weight of the container with and without CO_2. The pressure drop (Δp) in the storage bulbs was recorded after removing the CO_2 gas. The volumes of the storage bulbs calculated from the gas law were 5.94 ± 0.01 ℓ and 5.65 ± 0.01 ℓ.

Reaction Kettle Assembly

The reaction kettle (C in Fig. 1) has a lower part, a thick-walled cylindrical flask, connected to an upper part with an O-ring joint. The lower part contains a nickel dish, which serves as a metallic liner in the reaction zone (Fig. 2). The top of the reaction kettle has three inlets: two 28/15 ball joint sockets and one 3/8-in. glass-to-Kovar graded seal. A glass finger for the introduction of sodium and an electric heater are connected to the reaction kettle through the two sockets; the graded seal in combination with a Swagelok fitting is used to insert a thermocouple into the reaction (Fig. 3). The top of the kettle also has two side arms with stopcocks, one for connecting the kettle with the vacuum line and the other for connecting to the SiF_4 storage bulbs. All connectors and stopcocks are greaseless. After the reaction, the nickel dish containing the reaction products is removed for analysis of the reaction products.

Clean Sodium Generation

To obtain oxide-free sodium for the reaction with SiF_4 in Eq. (1), a glass finger (shown in Fig. 4) was constructed to fit one of the 28/15 ball joints in the top of the kettle (Fig. 2). It is essentially a narrow cylindrical funnel within a tube terminating in a 28/15 ball joint. Sodium chunks packed in this finger are held in place by a tungsten wire mesh, and the top of the finger is capped with an O-ring joint. In operation, the sodium finger is connected on the top of the reaction kettle (1 in Fig. 5) with a continuous vacuum applied through the kettle. The glass finger is heated externally to melt the sodium, and clean drops of sodium are collected in the reaction kettle. The oxide scum is retained by the wire mesh. From the weight difference of the glass finger before and after the reaction, the amount of clean sodium (typically, several grams) introduced into the reaction kettle is determined.

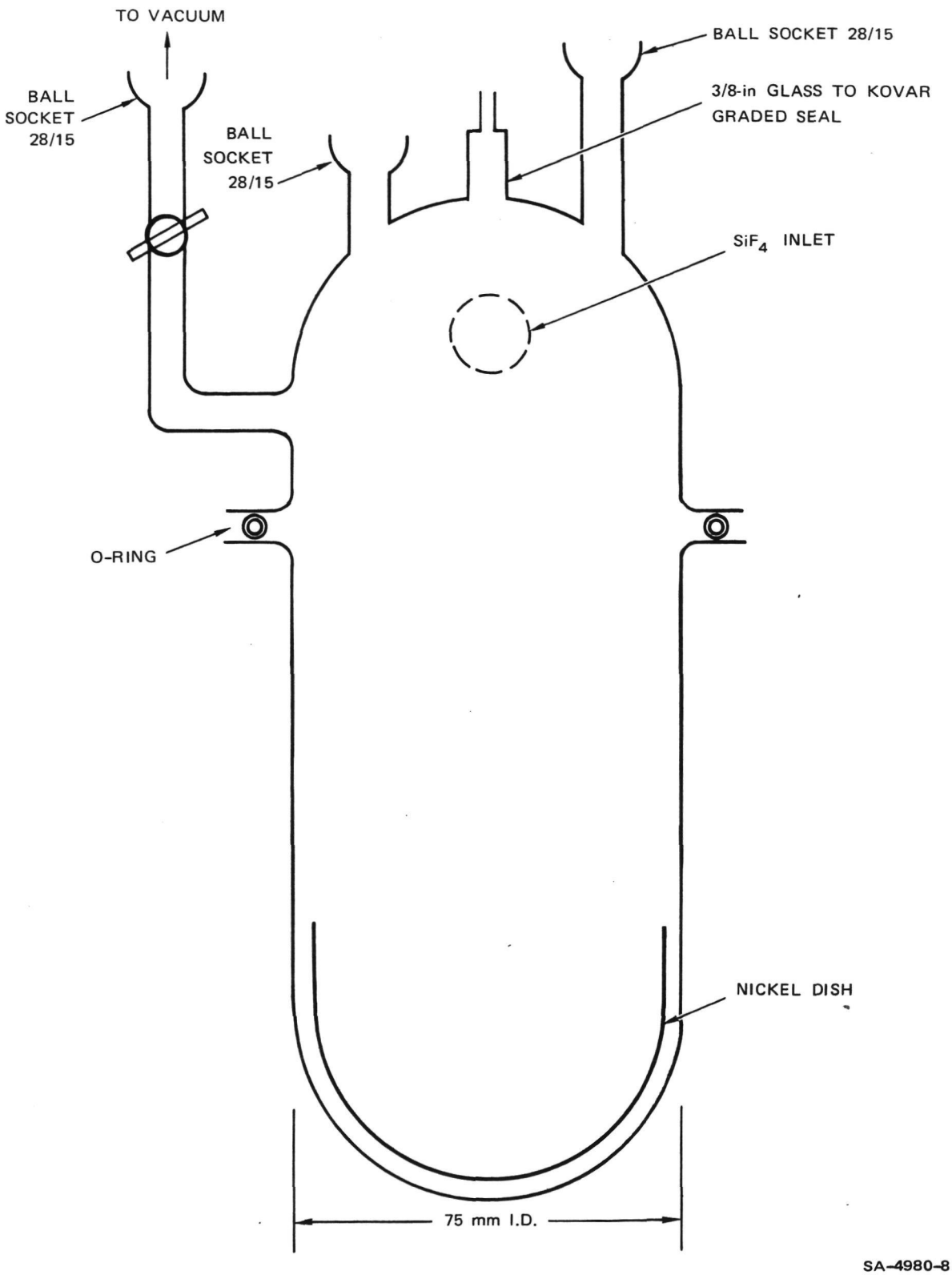


Figure 2

REACTION KETTLE

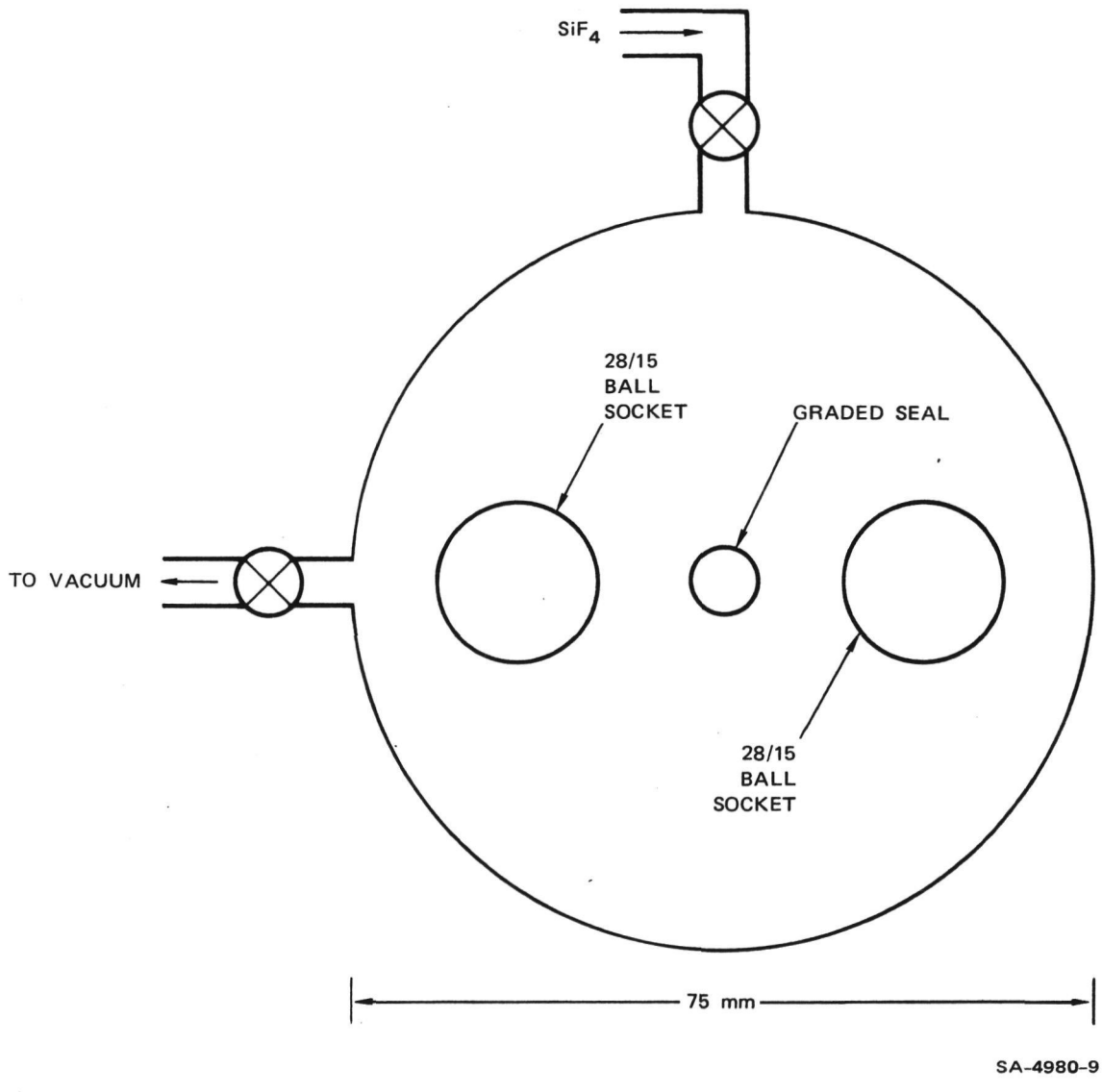


Figure 3

TOP VIEW OF REACTION KETTLE

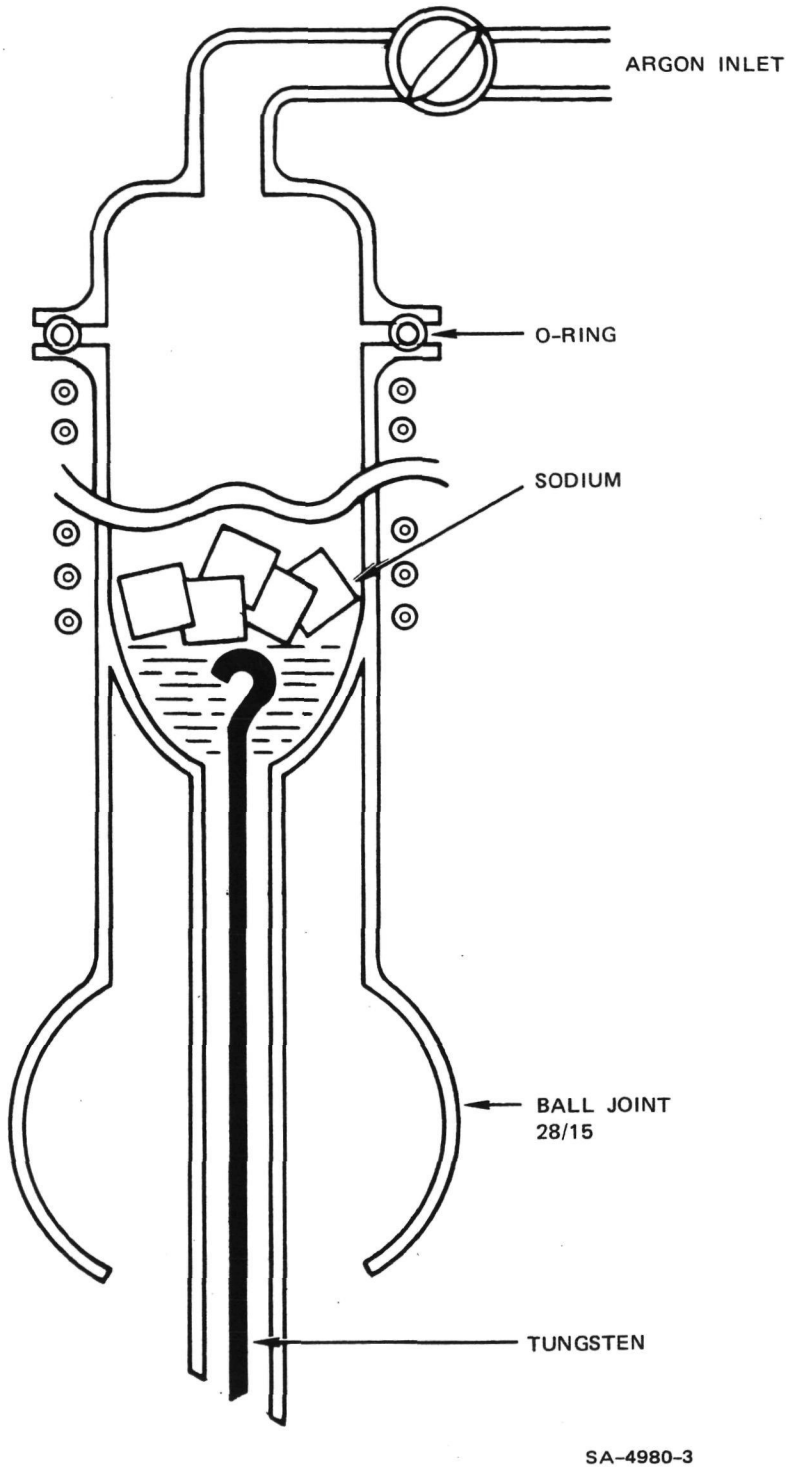


Figure 4

SODIUM FINGER

Figure 5

DETACHABLE REACTION KETTLE ASSEMBLY

(1) Sodium Finger

(2) Thermocouple Inlet

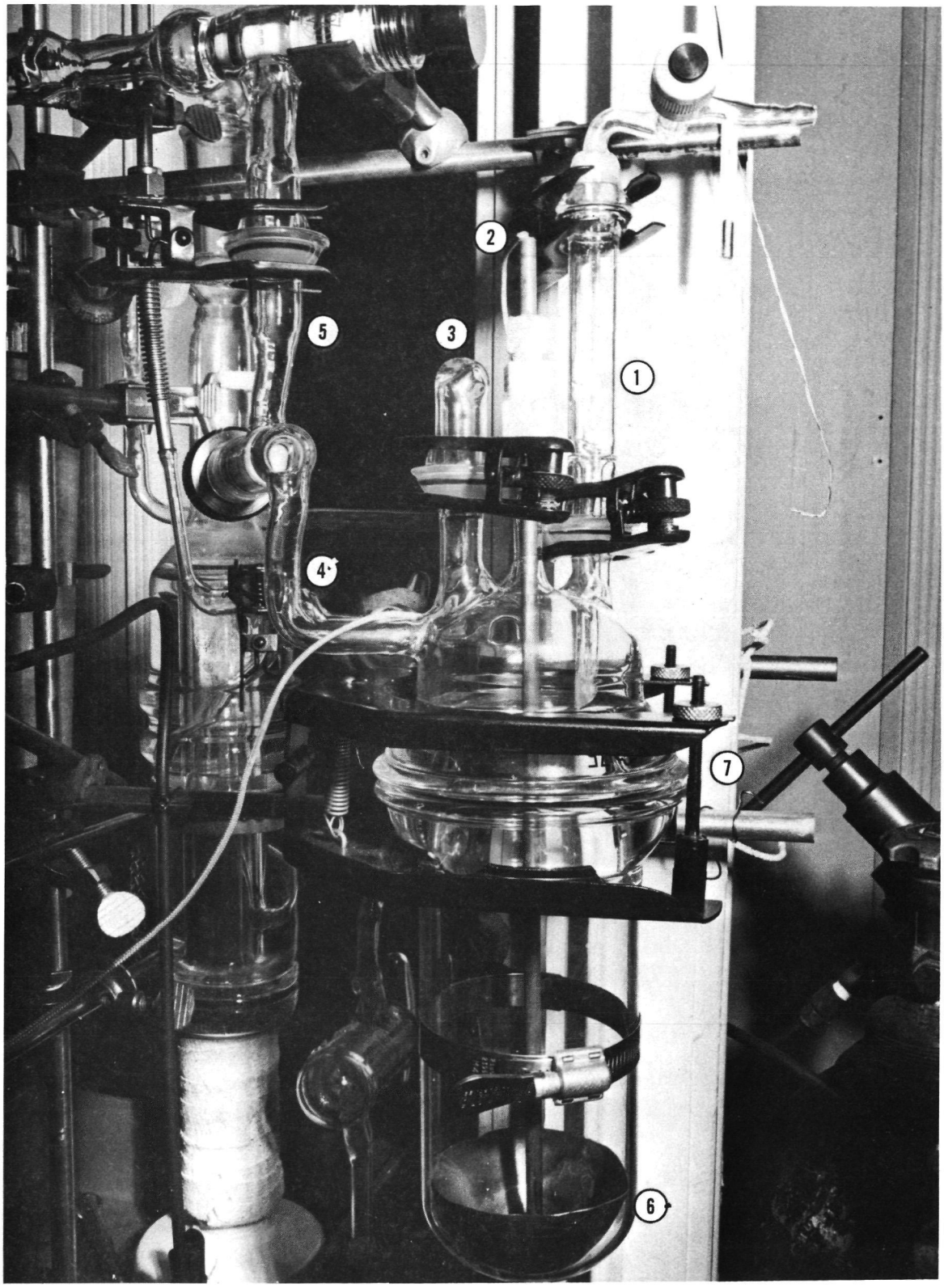
(3) Electric Heater Inlet

(4) Side Arm Connection to Vacuum Line

(5) Side Arm Connection to SiF_4 Storage

(6) Nickel Dish

(7) O-ring Joint



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To carry out the reaction in Eq. (1), the kettle--fitted with the glass finger containing sodium chunks and a thermocouple--was connected to the vacuum line (C in Fig. 1). SiF_4 storage bulbs were connected to the reaction kettle. The kettle was evacuated to a vacuum of less than 10 μHg and the glass finger heated externally to provide a pool of sodium around the thermocouple inside the nickel dish at the bottom of the reaction kettle. The sodium obtained in this manner was clean and free of any oxide coating. The vacuum line was cut off and the SiF_4 storage was opened to the reaction kettle. The pressure and the temperature of SiF_4 in the combined volume of the kettle and the storage bulbs were recorded. The reaction kettle was slowly heated externally while the temperature was continuously recorded. In a typical reaction sequence after the melting of sodium at 98°C, its surface was observed to tarnish followed by the growth of a distinctly black coating. As temperature increased, the entire sodium pool suddenly glowed at a dull red heat as the reaction rapidly spread. This stage of the reaction was marked by a sudden increase in the trace of the temperature of the reactants and a simultaneous drop in the pressure of SiF_4 (Figure 6). The reaction kettle was allowed to cool to the temperature at which the pressure of SiF_4 was recorded initially. The overall change in SiF_4 pressure was recorded, and the number of moles of SiF_4 consumed in the reaction was calculated as $\Delta n = \frac{V\Delta P}{RT}$. The reaction kettle was evacuated to remove unused SiF_4 and detached from the vacuum line. The reaction products in the nickel cup were weighed and analyzed. In computing the number of moles of SiF_4 consumed in the reaction, the volume used was that of the storage bulb plus that of the reaction kettle. As shown in Fig. 6, reaction of SiF_4 with sodium proceeds rapidly at 152°C. As different sections of the sodium pool react, the temperature increases in bursts until the main pool sustains a continuing reaction, ultimately rising rapidly to 452°C.

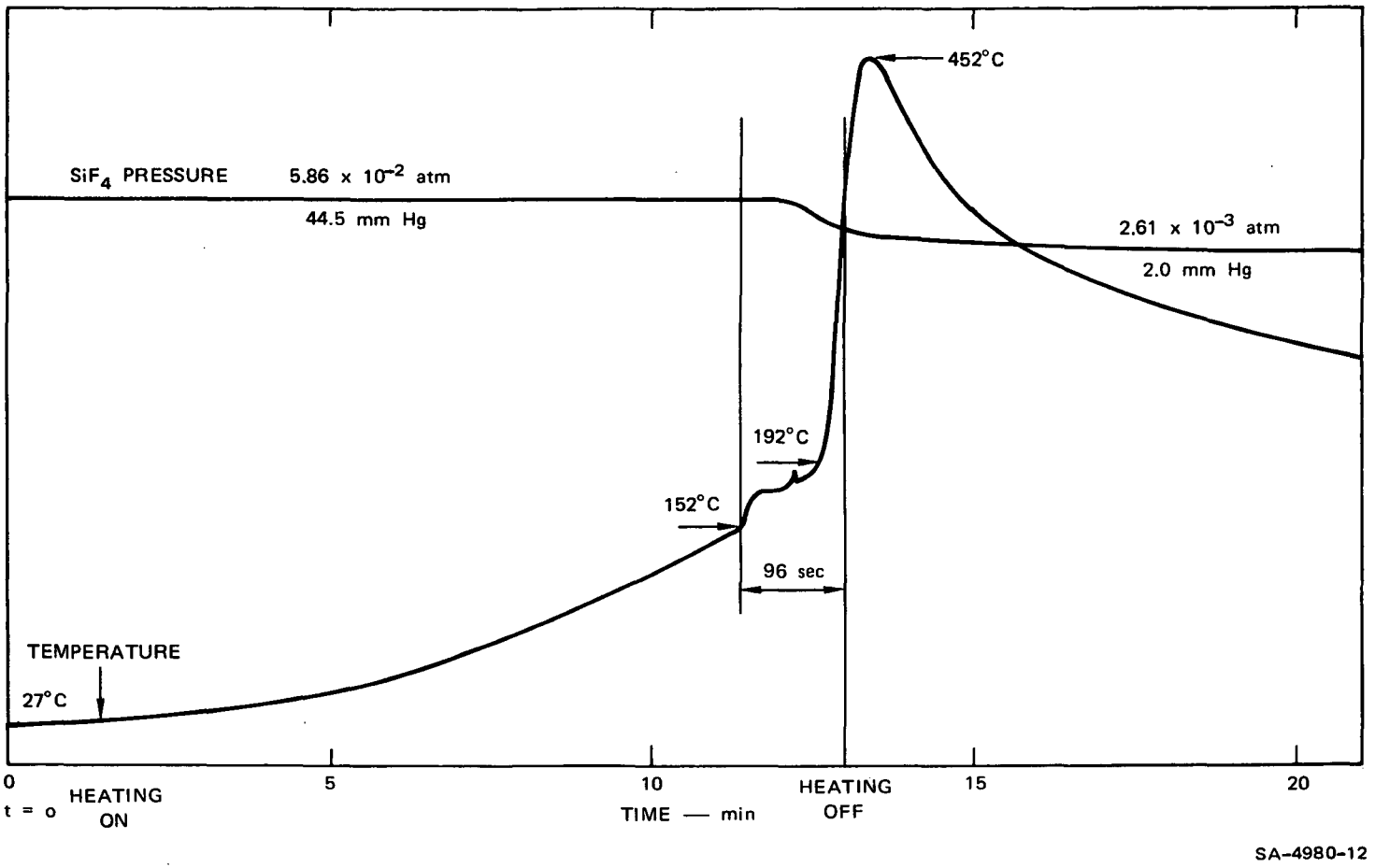

Figure 6

REACTION TEMPERATURE AND PRESSURE VS. TIME

ANALYSIS

The reaction products of Eq. (1) were analyzed by X-ray diffraction to identify the various phases present. Three phases were detected: NaF, Na_2SiF_6, and Si. To separate silicon from the fluorides of sodium, a weighed amount of the products was mixed with water and heated, with stirring. The dissolved sodium compounds were filtered and silicon was collected as insoluble residue. From examination of the reaction products by scanning electron microscope, there is evidence that the silicon thus obtained was coated with SiO_2. The silicon yield was estimated from the weights of reactants and products as shown in Table 1 in the following section.

The silicon obtained after filtration was analyzed for impurity content by emission spectroscopy. The results are shown in Table 2. Studies are continuing on the use of nuclear magnetic resonance to give a quantitative measure of NaF and Na_2SiF_6 in the reaction products of Eq. (1).

RESULTS

The weights of the reactants and products for three runs are listed in Table 1. Important points are as follows:

1. The mole ratio Na/SiF_4 is always less than 4, suggesting that SiF_4 gas being consumed in the reaction is more than the stoichiometric amounts required for Eq. (1). This can be accounted for by the formation of Na_2SiF_6.

2. The amount of the insoluble material weighed as silicon after washing the reaction products with water is greater than the theoretical amount of silicon expected, calculated on the basis of moles of Na used. This observation suggests that some of the silicon becomes oxidized to SiO_2 during washing.

3. The semiquantitative analysis of silicon samples by emission spectroscopy (Table 2) shows that the major impurity, as would be expected, is sodium. The amount of sodium in the product can be decreased by improved methods of leaching sodium fluorides. No ready explanation is available for the presence of boron in sample #2(1) and its absence in others. Transition metals known to degrade the efficiency of silicon solar cells, such as titanium, vanadium, zirconium, and chromium, were not observed in the spectrographic analysis; if they are present, their amounts must be less than 10 ppm.

Table 1

WEIGHTS OF REACTANTS AND PRODUCTS

$SiF_4 + 4Na \rightarrow Si + 4NaF$

Run	Amount of Sodium Reacted		Amount of SiF_4 Used		Mole Ratio Na / SiF_4	Total Weight of the Reactants (grams)	Weight of Reaction Products (grams)	Weight of Silicon Obtained (grams)	Theoretical Weight of Silicon * (grams)
	grams	moles	grams	moles					
2(1)	0.656	0.0285	1.0608	0.0102	2.79	1.717	1.594	0.230	0.199
2(2)	0.926	0.0403	1.2792	0.0123	3.27	2.205	2.183	0.334	0.281
2(3)	0.384	0.0602	1.820	0.0175	3.44	3.204	3.146	0.528	0.421

* Theoretical weight of silicon calculated on the basis of weight of sodium used, as $\frac{\text{moles of Na} \times 28}{4}$

Table 2

EMISSION SPECTROGRAPHIC ANALYSIS OF SILICON
(Semiquantitative)

Element	Percent Impurity in Silicon			
	Run 2 (1)	Run 2 (2)	Run 2 (3)	Run 2 (3)a*
Al	0.005	0.001	< 0.001	< 0.001
Na	1.500	1.000	0.75	1.25
Ca	0.003	0.004	0.006	0.006
Mg	0.002	0.002	< 0.001	0.001
Ba	< 0.001	0.001	< 0.001	< 0.001
B	< 0.01	-	-	-
Cu	< 0.001	0.001	< 0.001	< 0.001
Fe	< 0.005	< 0.005	< 0.005	< 0.005
Ti	< 0.001	< 0.001	< 0.001	< 0.001
V	< 0.001	< 0.001	< 0.001	< 0.001
Cr	< 0.001	< 0.001	< 0.001	< 0.001
Zr	< 0.001	< 0.001	< 0.001	< 0.001

* Sample nos. 2(3) and 2(3)a are duplicates from the same lot. Results should be compared for an internal check on the analysis.

DISCUSSION

The method of making silicon by reducing SiF_4 gas with sodium Eq. (1) has other features of practical interest.

1. The reaction initiates at temperatures lower than 175°C, liberates a large quantity of heat, and continues to completion.

2. Silicon thus obtained is in the form of a fine powder, which offers a large surface area for the disproportionation reaction in Eq. (2) to be used for further purification.

3. On the basis of preliminary experiments, the reaction rate appears to be very much affected by the partial pressure of SiF_4 gas; therefore, it is expected that variation of the partial pressure of SiF_4 can be used for control of the reaction rate. When the reaction is carried out with a pressure of SiF_4 at less than 0.5 atm, the silicon obtained is relatively granular; with the SiF_4 pressure near 1.0 atm, the reaction proceeded very vigorously, yielding silicon in a very fine powder form.

4. In all these experiments, the reaction efficiency estimated from mass balances is close to 90% for Eq. (1).

5. The emission spectrographic analysis shows that the silicon thus obtained has higher purity than the conventionally used metallurgical grade. The present experiment was carried out with SiF_4 gas straight from the cylinder, and the sodium was used without rigorous purification. Nevertheless, the silicon obtained contains no metallic impurities known to

be detrimental to solar cell efficiency. It is confidently expected that the levels of impurities observed can be further reduced by purifying the SiF_4 and by making modifications to the process of removing silicon from the reaction products.

6. The separation of silicon from the reaction products by leaching the sodium fluoride with water poses some problems. First, washing with water oxidizes the surface of finely divided silicon to SiO_2; second, a trace amount of unreacted sodium in contact with water can form sodium hydroxide, which in turn, tends to dissolve some of the silicon in hot aqueous solutions.

CONTINUING STUDIES

1. We plan to try some other methods of separating silicon from the reaction products, particularly separation of fluorides by fusion. Since the step in Eq. (2) requires the silicon to be heated to 1100°C or greater, it is reasonable to consider heating together all the reaction products from Eq. (1). At around 600°C, Na_2SiF_6 will decompose to give NaF and SiF_4 gas. The SiF_4 gas will react with any unreacted sodium to form silicon and NaF. On further heating, NaF will melt at 993°C and can be separated as a liquid phase. The hot silicon left behind can be heated to 1100°C to perform Step 2 of the process.

2. Methods used to extract sodium fluorides will be studied as a means to minimize surface oxidation of product silicon. Nonaqueous solvents will be examined for suitability.

3. We will also carry out the Step 1 reaction at selected pressures of SiF_4 in the range of 0.01 atm to 1.0 atm.

4. The silicon samples will be analyzed by mass spectrometric methods to further determine the levels of impurities present in amounts less than 10 ppm.